Some Structures and Properties of Very High Molecular Weight Linear Polyethylene (Special Issue on Polimar Chemistry, VI)

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 47, No. 3, 1969

Some Structures and Properties of Very High Molecular Weight Linear Polyethylene

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Received May 6, 1969

The orientational structures of crystalline and noncrystalline chains for a very high molecular weight linear polyethylene ($\bar{M}v = 2.5 \times 10^6$), which was crystallized from the molten and stretched state maintaining the stretched length of the sample at constant, were investigated by birefringence and x-ray diffraction measurements. The stress-strain behavior at temperatures above the melting point, and the thermal shrinkage, the dynamic mechanical property and the melting behavior of the sample crystallized in such a way were also studied.

This polymer could be stretched without breaking, behaving like rubbery materials at the molten state, as we have observed for a crosslinked polyethylene. The orientational structure of the crosslinked polyethylene, which was crystallized from a highly stretched and molten state, has been analyzed to be composed of highly oriented crystalline chains and little oriented noncrystalline chains. An analogous orientational structure to the above mentioned crosslinked polyethylene was again found for the present sample polymer, when it was prepared in the same way as taken for the crosslinked polyethylene.

This characteristic structure of the sample was well reflected in the behavior of the thermal shrinkage, suggesting a very high thermal stability of crystals in the sample crystallized in such a way. This high thermal stability of the crystals was confirmed by determining the melting point and the temperature dependency of dynamic mechanical properties of the sample.

I. INTRODUCTION

Polyethylene whose molecular weight is more than about 1,000,000, even if it has perfect linear molecular structure, will not flow so easily even in the molten state at much higher temperatures than its melting temperature and may behave itself like rubbery materials to some extent, because the number of the so-called entangled points per a molecular chain is considered to be very large owing to its huge molecular weight. If it behaves like rubbery materials at the molten state, it must be highly extensible without breaking at the molten state. This allows us to study the stretching mechanism of a linear polymer at non crystalline state, the crystallization behavior from the oriented molten state, and the fine structure and property of the polymer crystallized from the oriented molten state as well.

We have studied the crystallization mechanism from oriented molten state of a slightly crosslinked polyethylene as well as the fine structure and some mechanical properties of the sample crystallized in such way.[1~3]

In this paper, we investigate some structures and properties of a very high

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molecular weight linear polyethylene which is crystallized mainly from the stretched and molten state. This polymer is preferred to study the oriented crystallization rather than the crosslinked polyethylene in some points, because it is more homogeneous than the crosslinked sample which contains some crosslinked points. But the polymer necessarily must flow to some extent at the molten state and can not maintain the fixed state of the orientation.

II. EXPERIMENTALS

1. Sample

Hostalen (Höechst Co.) was used as a sample of very high molecular weight polyethylene. Its viscosity average molecular weight was determined as 2.5×10^6 from the intrinsic viscosity number of decalin solution at 135°C, according to Chiang's equation.[4]

$$[\eta] = 6.2 \times 10^{-4} M^{0.70}$$

The density at 30°C for the sample which was quenched into water of 10°C from the molten state at 165°C was 0.923 and the degree of the crystallinity calculated from the density was 54%.

The very excellent linearity of the molecules for the Hostalen was quantitatively confirmed by infrared spectroscopies with use of 1378 and 1370cm^{-1} bands according to Miller and Other's method.[5]

2. Mechanical properties

The static tensile properties of samples were measured at various temperatures by Tensilon UTM-2 (Toyo Sokki Co.). The length, width and thickness of the samples were 40mm ,1mm and 0.12mm, respectively, and the elongation rate of the sample was 250%/min.

The temperature dependence of the dynamic modulus E' and dynamic loss E'' for samples at a constant frequency of 110cps. were obtained by Vibron DDV-2 (Toyo Sokki Co.).

3. Birefringence and x-ray diffraction

The change in the birefringence with stretching and temperature was measured with a polarizing microscope by examining the stretched sample between crossed nicol prisms. The amount of retardation was determined by using Berek's compensator.

The wide angle x-ray diffraction pattern for the stretched sample of 0.2-0.3mm thickness was obtained by Toshiba ADG-101 diffractometer with the use of nickel-filtered copper radiation.

4. Thermal shrinkage and melting point

The change in the length of the stretched sample in the direction of stretching with the continuous raise of temperature was observed with a cathetometer. The one end of the sample of 30mm length, 1mm width and 0.2-0.3mm thickness was fixed with a clamp and on the another free end a load of 10g/mm^2 was supplied.

Melting points of unstretched and stretched samples which were cooled from mol-

ten isotropic or stretched state to room temperature, keeping the stretched length of the sample in the latter case, were determined from specific volume-temperature curve using a dilatometer with a capilary of 0.5mm diameter. The rate of the raising temperature was 1°C/day at the near temperature to the melting point (130-145°C). The temperature of oil bath was controlled in the accuracy of $\pm$ 0.05°C.

III. RESULTS AND DISCUSSION

1. Tensile properties

Stress-strain curves at the temperature from 25°C to 155°C were shown in Fig.1. In the curves obtained at above the melting point (145-155°C), yield points can not be observed and also in the curve at 155°C, the stress does not change over the range of elongation. On the other hand, the largest value of elongation at break is obtained in the case of measurement at 135°C and the elongation at break diminishes with the lowering or raising of temperature from 135°C.

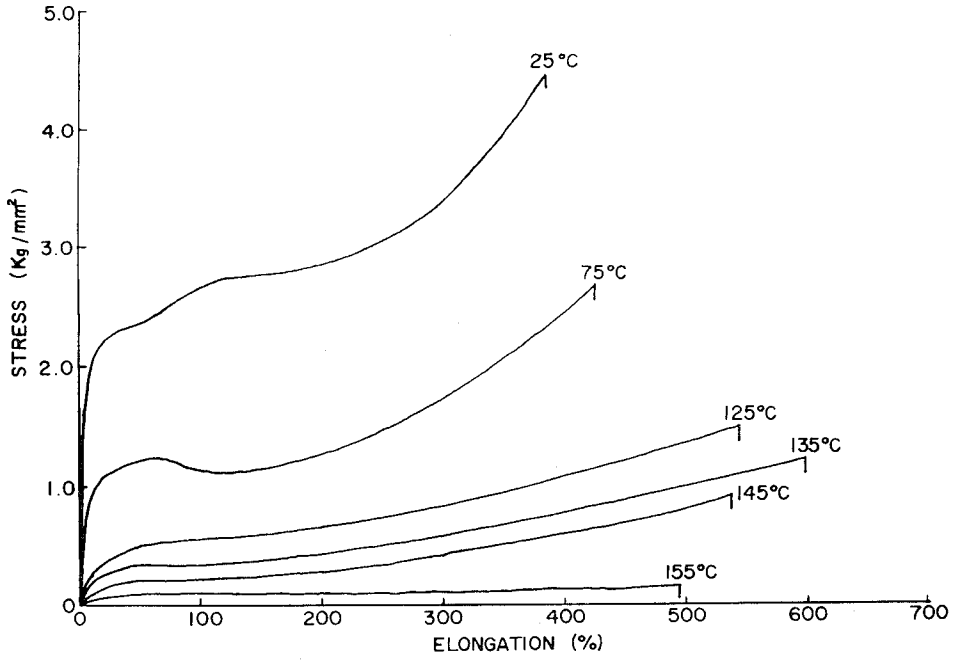

Fig. 1. Stress-strain curves for the Hostalen at various temperatures.

Linear polyethylene whose molecular weight is in the order of 10^5 or less can not be stretched at temperatures above 135°C without breaking down in the usual time scale of stretching. But in this case for very high molecular weight polyethylene, stretching without breaking is possible at the temperatures above 135°C and even at 155°C elongation can be achieved to 500% without breaking and with some tensile forces.

These facts suggest that the Hostalen used here does not flow easily and can be

oriented at the molten state within the experimental time scale, because the entangled points in such a high molecular weight polyethylene may behave like crosslinked points in vulcanized rubbery materials. But the fact that the value of elongation at break diminishes with the increase of temperature above 135°C may indicate that the flowing occurs much more as the temperature is raised from 135°C.

The features of curves at the temperatures above the melting point are not as expected theoretically for ideal rubber, except for the curve at 155°C. According to the theory for ideal rubber[6] the stress must be rapidly increased in the range of low stretching ratio and as further increase of stretching ratio, the slope of the curve gradually decreases and reaches a plateau line. This is true in this case only for the curve at 155°C and at another temperature above its melting point, curves are different from the theoretical curve for ideal rubber and the stress is continuously increased by elongation at above 200%, but in the region of elongation below 200% the curves at 125, 135 and 145°C are quite similar to the curve for ideal rubber. This feature of stress - strain curve for the Hostalen at the high temperature seems to be similar to the curve for crystallizable rubbery materials. The difference between the curve for ideal

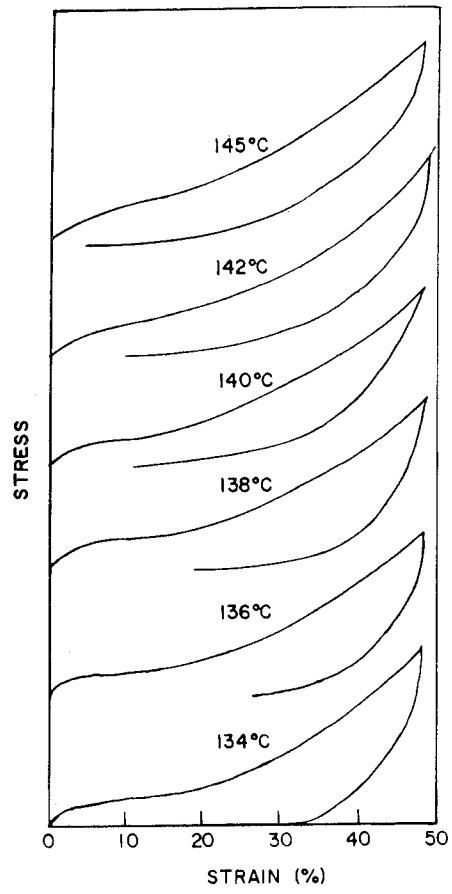

Fig. 2. Stress-strain hysteresis curves for the Hostalen at various temperatures.

rubber and the curves for the Hostalen at high temperature above its melting point may be occurred from the crystallization of the sample at higher elongations.[7]

In order to crystallize a polymer at a temperature above its normal equilibrium melting temperature, it should be required that the molecular chains of the polymer are oriented before crystallization, because the melting temperature should be increased with the orientation of the molecular chains. The characteristic behavior of the Hostalen accompanying crystallization and orientation will be shown also in the stress-strain hysteresis curve at various temperatures as shown in Fig. 2.

These hysteresis curves were obtained by stretching film samples to 50% the original length and then releasing those to the original length between clamps. It is evident from the figure that the curves at 140-145°C show good elastic recovery, but some viscous flows occur in the experimental time scale. As the temperature is descended, the recoverable property of samples is decreased. This behavior may be due to a partial crystallization of the sample during stretching and to restricted mobilities of molecular chains caused by the stretching. It must be noted that when crystallites formed here are fused by rising temperature the stress will increase again.

Another evidence for the rubbery elastic property at the molten state of the Hostalen is a temperature dependency of stress for stretched samples at a constant length. In Fig. 3, change in stress for 6 times stretched sample with the increasing and decreasing of temperature is shown. Stress decreases continuously up to about 120°C and after going through a minimum point increases to about 40kg/cm² at 145°C and by cooling, stress changes symmetrically to the case of heating. On the contrary, for ideal rubbery material, stress increases linearly with the raising of temperature under constant stretching ratio[6] and this is also experimental fact observed for vulcanized natural rubber[8]. For the Hostalen, a similar behavior could be observed at the temperature range from 130 to 145°C as shown in Fig. 3, but in this case it may be partially due to the melting of oriented crystallites. The stress decrease in the range from room temperature to about 120°C should be attributable to the thermal expansion of the sample to the direction of stretching and some stress relaxation.

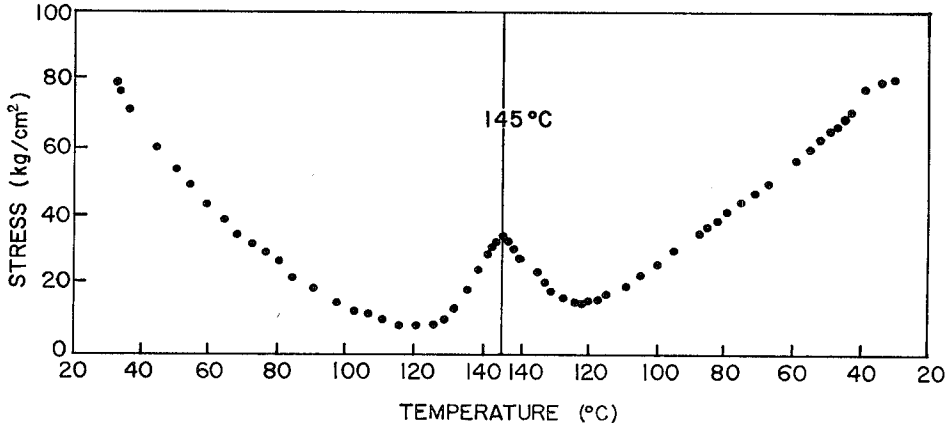

Fig. 3. The change in stress with heating and cooling for 6.0 times stretched sample of the Hostalen at constant length.

The conclusion obtained from these tensile properties is that the Hostalen has a rubbery elasticity at temperatures above its melting point, even though there are some deviation from the behavior of ideal rubber because of stress relaxation by flowing and the crystallization by deformation.

2. *Molecular orientation by stretching*

As entangled points in very high molecular weight polymer such as Hostalen behave like crosslinked points, the Hostalen can be stretched and oriented at molten state like a crosslinked polyethylene and also it is expected that the very characteristic orientational structure which was found in a slightly crosslinked polyethylene[2] crystallized from stretched and molten state may be observed in the case of the Hostalen.

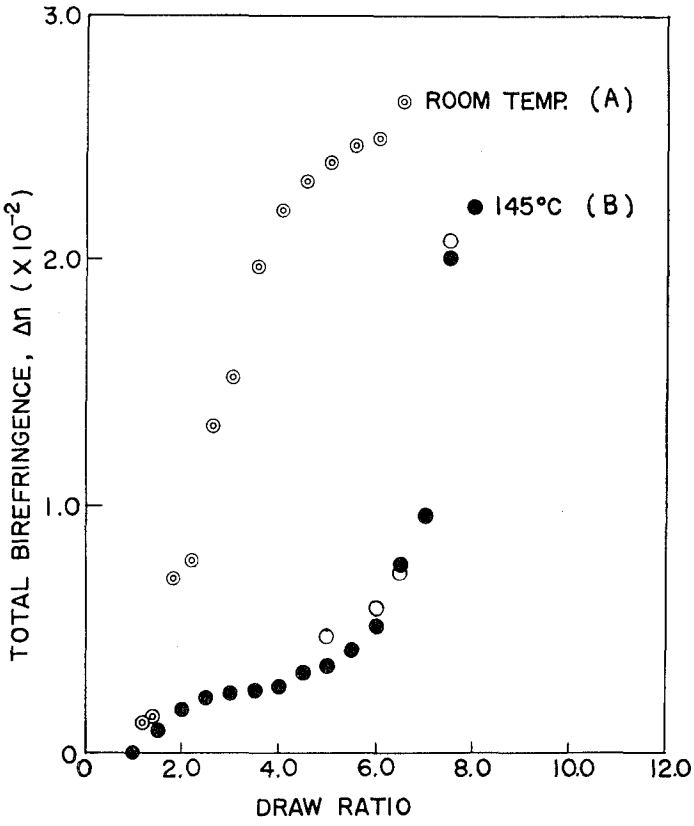

Fig. 4. The change in total birefringence with stretching at 145°C (B). Curve (A) is the data after the colling to room temperature from the stretched state at 145°C.

The change in total birefringence, Δn with the stretching at 145°C is shown in Fig. 4-B. In this case, if we neglect effects of form and stress birefringence, total birefringence is equal to the birefringence of noncrystalline molecular chains, Δa, unless any crystallization occurs. For example, we can obtain the value of Δa for 4.0 times stretched sample at 145°C as 0.0026. The value of Δa for fully extended noncrystalline polyethylene chain has been estimated as 0.0428 by Stein[9] and if we use this value we can obtain a value of 0.061 as orientation factor of noncrystalline

chains, fa, from the equation of $\Delta a = 0.0428 \times fa$. If we assume that the noncrystalline chains which have a orientation factor of 0.061 crystallize perfectly, maintaining the same orientation factor, namely the orientation factor of the formed crystals is 0.061, the value of crystalline birefringence, Δc, is equal to Δn and $\Delta c = \Delta n = 0.0574 \times 0.061 = 0.0035$, where 0.0574 is the value of the birefringence for fully extended crystalline chain.[9] But as shown in Fig. 4-A, the total birefringence after the cooling to room temperature for 4.0 times stretched sample is 0.0223, which is significantly higher than as expected above. The difference will be due to the fact that the orientation factor of the crystallites formed during cooling is much higher than expected from the molecular state before crystallization. We have obtained x-ray diffraction pattern for this cooled sample to confirm this suposition and obtained the information of crystalline orientation, and the pattern is shown in Fig. 5.

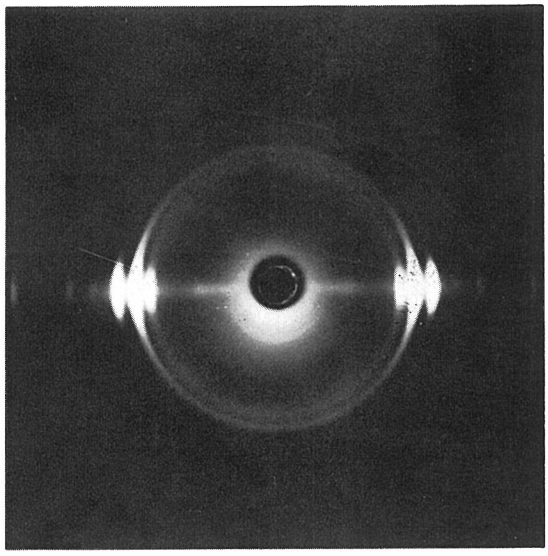

Fig. 5. The wide angle x-ray diffraction pattern of the Hostalen stretched at 145°C to 4.0 times and then cooled to room temperature.

It is apparent from the x-ray diffraction pattern that the degree of crystalline orientation to the direction of stretching is surprisingly large and the orientation factor can be qualitatively estimated as about 0.7. The degree of the crystallinity from the density for the cooled sample was about 60%. The value of crystalline contribution term in the total birefringence, calculated using these valuse of orientation factor and the degree of crystallinity was $0.0574 \times 0.7 \times 0.6 = 0.0241$. This value coincides well with the observed value of total birefringence. This result may suggest that, in the crystallization from molten stretched state, crystals are formed with highly orientating the chain axis of the crystals to the direction of stretching, even though the degreee of orientation of noncrystalline chains is small at the starting point. This conclusion is not only obtained for the case of draw ratio 4.0, but also applicable to every draw ratio examined here, and consistent with the conclusion which had been obtained from the study of oriented crystallization for a slightly crosslinked poly-

ethylene.[2)]

In Fig. 4, it is shown that the total birefringence at 145°C is increased rapidly with the increase of draw ratio above 5.0 times. This may be well interpreted by the crystallization with stretching, namely the melting point of the sample stretched to more than 5.0 times becomes higher than about 145°C and then crystallization occurs under orientation of molecules which results in the increase of birefringence. On the other hand, low values of the birefringence at low draw ratios at where crystallization does not occur may suggest that there occurs some flow by which the molten molecular chains move as they return to the initial random state.

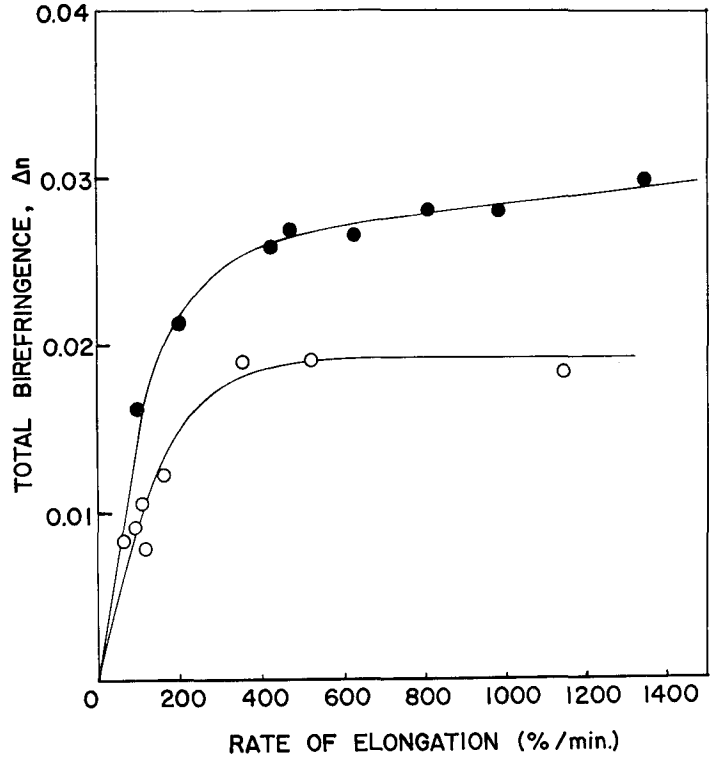

Fig. 6. The variation of total birefringence of the Hostalen with the rate of elongation. (●) ; Flongation at 145°C, (○) ; Elongation at 150°C.

The effect of rate of stretching on the birefringence was examined. In Fig. 6, the variation of birefringence for the sample stretched to 5.0 times at 145°C, with the change of the rate of stretching from 2.0 times/min to 15.0 times/min is shown. This figure indicates that molecular orientation is significantly depended on the rate of stretching in the range to about 5.0 times/min. From this fact, it is obvious that, in a low rate of stretching, stretching must be carried out accompanying remarkable disorientation of noncrystalline molecular chains.

3. Thermal shrinkage

The configurational feature of oriented polymer is closely related to the thermal shrinkage or thermal expansion behaviors, and the characteristic feature of the oriented

state of the polymer is usually well reflected to these behaviors. In Fig. 7, thermal shrinkage curves for the films of the Hostalen stretched at 80°C and 145°C are shown. The most remarkable feature which can be seen in this figure is the difference between the curve for the sample stretched at 80°C and the one for the sample stretched at the molten state of 145°C and then cooled to room temperature under the constant length of stretched state. The former sample begins to shrink at about 40°C and continuously shrinks to about the melting point, but the latter sample does not shrink up to 125-130°C at where the partial fusion of oriented crystals may begin, and then going through this temperature the sample shrinks very rapidly. These shrinkage curves are quite similar to the curves obtained at same conditions for crosslinked polyethylene,[1] though there exists some differences duing to the flow in the case of the Hostalen. The characteristic feature of shrinkage for samples of the Hostalen can be interpreted in the same manner with the case of crosslinked polyethylene. The result obtained here suggests as in the case of crosslinked polyethylene that the uncrystallized molecular chains in the latter sample are not oriented or disoriented during the crystallization under stretched state, and the thermal stability or the degree of the perfection of the oriented crystals are very good comparing to the sample stretched at a temperature below its melting point. The unoriented or lowly oriented state of uncrystallized chains in the sample crystallized from the molten stretched state can be also supported by the result of birefringence for this sample. As discussed in the last section, for example, the total value of the birefringence for the sample which was 4.0 times stretched

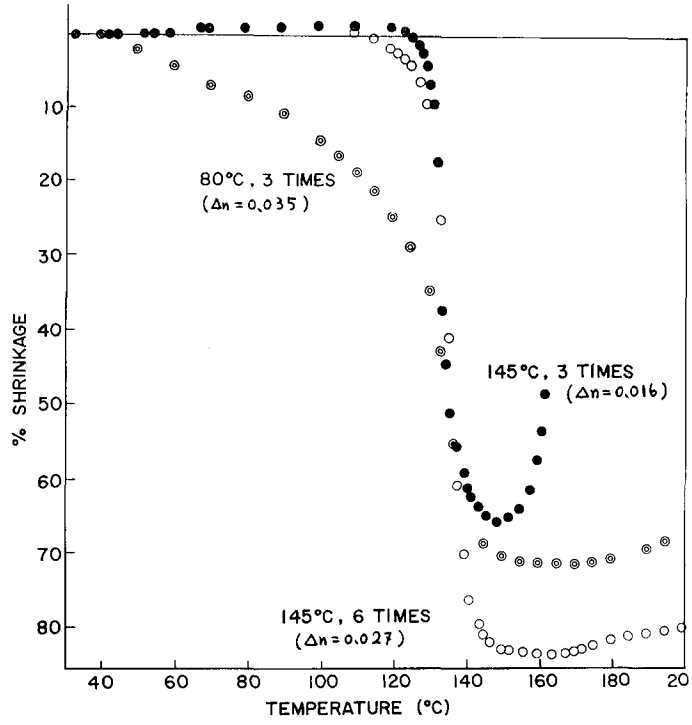

Fig. 7. Thermal shrinkage curves for the Hostalen stretched at 80°C and 145°C.

at 145°C and then cooled to room temperature was almost occupied by the birefringence of oriented crystals. This result also suggest that the uncrystallized chains is disoriented during the oriented crystallization of the polymer.

As we discussed in previous paper[1] these shrinkage behavior of the Hostalen sample which was crystallized from molten stretched state may be a reflection of the configurational feature of the sample which is composed of highly oriented crystalline chains and unoriented or little oriented noncrystalline chains.

4. Dynamic mechanical properties

In Fig. 8 and 9, temperature dependencies of dynamic modulus, E', and dynamic loss, E'', for various stretched samples of the Hostalen are shown respectively. The largest values of E', and E'' are obtained over the whole range of temperature for the sample strecthed at 145°C and also the values for the sample stretched at 120°C are larger than that for the sample strecthed at 80°C. The values of birefringences for the samples stretched at 120°C and 145°C were 0.040 and 0.028 respectively, and the value for the sample stretched at 80°C was nearly equal to the value for the sample stretched at 120°C. On the other hand, densities at 30°C for samples stretched at

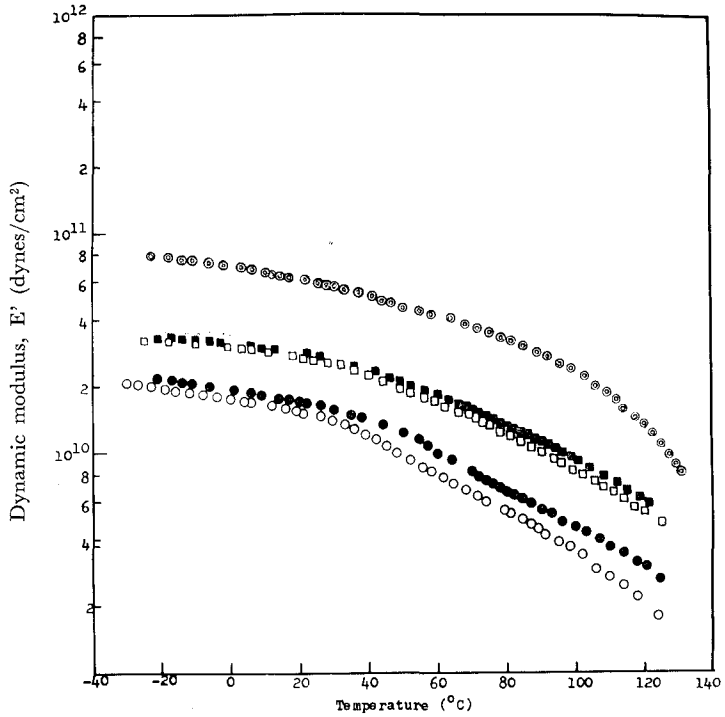

Fig. 8. Temperature dependency of dynamic modulus for the films of the Hostalen stretched at various temperatures.
(○) ; stretched at 80°C to 5.0 times.
(●) : stretched at 80°C to 5.0 times and then annealed at 100°C for 3 hours.
(□) ; stretched at 120°C to 6.0 times.
(■) ; stretched at 120°C to 6.0 times and then annealed at 120°C for 3 hours.
(◎) ; stretched at 145°C to 6.0 times and then quenched to room temperature under the constant length of stretched state.

145, 120 and 80°C were 0.9535, 0.9400 and 0.9278g/cc respectively as shown in Table 1. It may be concluded from these data that the difference in the values of E' and E'' between three stretched samples is not only due to the difference in the degree of the molecular orientation, but to the difference in the degree of the crystallinity.

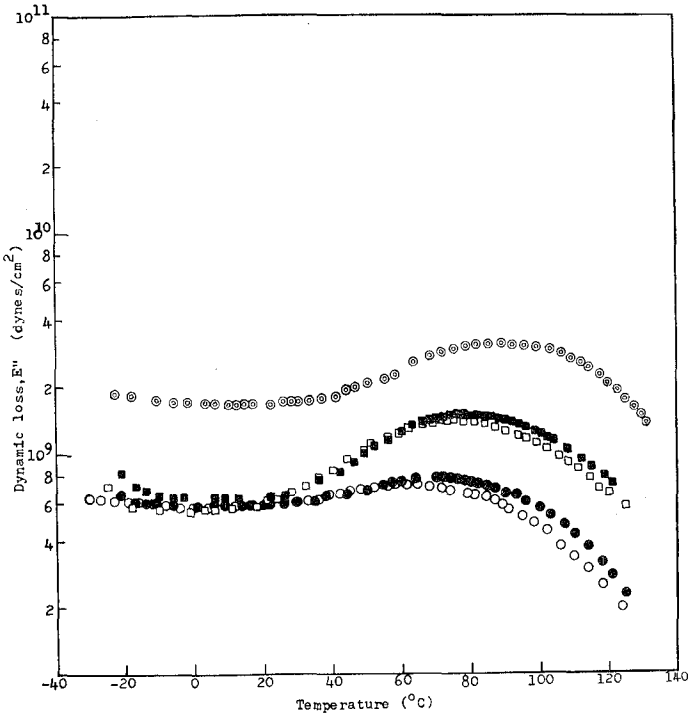

Fig. 9. Temperature dependency of dynamic loss for the films of the Hostalen stretched at various temperatures. Symbols in the figure are the same with those in Figure 8.

The absorption, in E''-temperature curve, which appears in the temperature range from 60°C to 120°C is usually assigned to the molecular motion in the crystalline phase and is related to the degree of the crystallinity, the degree of orientation of the crystals and the degree of perfection of the crystals.[10~12] The significant difference between the three absorption curves can be observed in the position of the absorption which can be characterized by the peak temperature (Tc). The peak temperature is shifted to higher temperatures with the raising of the stretching temperature and this result can be interpreted by the increasing of the degree of crystallinity, but it is difficult to consider that the shift is only attributed to the difference in the degree of crystallinity, because rather large shift is observed in spite of the very small difference in the densities (see Table 1).

In this case, it is more suitable to consider that the higher value of the peak temperature must be arised much more from the higher thermal stability or higher degree of perfection of crystals than the higher degree of crystallinity of the sample.

The value of the peak temperature for polyethylene which was obtained by other

Table 1. Dynamic Mechanical Properties of Stretched Hostalen

Stretching temperature (°C)	Draw ratio (times)	Density at 30°C (g/cc)	$E' \times 10^{-10}$ at 20°C (dynes/cm^2)	$E'' \times 10^{-9}$ at Tc (dynes/cm^2)	Tc (°C)
80	5.0	0.9249	1.51	0.73	64
80[a]	5.0	0.9278	1.60	0.79	72
120	6.0	0.9350	2.70	1.40	75
120[b]	6.0	0.9400	2.80	1.48	79
145	6.0	0.9480	6.36	1.69	89
145[c]	6.0	0.9535	5.40	2.00	108
unstretched	—	0.9233	0.92	0.33	65

[a]) 3 hours annealed at 100°C.
[b]) 3 hours annealed at 100°C.
[c]) slowly cooled from 145°C to room temperature (5°C/hr)

authors under similar conditions of the measurement is about 70-90°C and we have also obtained the values in this range for many kinds of polyethylene. But the highest value of the peak temperature we have obtained was 97°C for a sample of linear polyethylene which was a fraction from Marlex-50.[1)] The viscosity average molecular weight of this fraction was 365,000 and the sample for the measurement was prepared by the isothermal crystallization at 129°C from the molten state of 165°C, for 20 days and the density of the crystallized sample at 30°C was 0.983 which is corresponded to the degree of crystallinity of 91.3%. As we have reported, the value of 97°C for Tc was also obtained for a slightly crosslinked polyethylene which was stretched to 16 times at molten state and then quenched to room temperature under the constant length of stretched state.[1)] For the Hostalen, the highest value of Tc was 108°C for a sample slowly cooled to room temperature from the molten stretched state, as shown in Table 1. From these results, it is confirmed again that the peak temperature does not simply depend on the degree of crystallinity. It must be noted also that the very stable crystalline structure, which is possible to be formed by the isothermal crystallization at the temperature near to the melting point for a very long time, could be obtained in a very short time like quenching in the case of oriented crystallization.

5. Melting temperature

It has been supposed from the thermal shrinkage behavior and dynamic mechanical property that the crystals formed from the stretched and molten state of the Hostalen have a excellent thermal stability. If this is true, it may be reflected to the melting behavior of the sample.

We have measured the melting temperature for samples of the Hostalen which were slowly cooled to room temperature from the isotropic molten state and from the 6.0 times stretched and molten state. The dilatometric melting curves for these samples are shown in Fig.10. The melting temperature of the sample crystallized from the stretched and motlen state was 140.5°C and this value is larger than the value for isotropically crystallized sample as 4.0°C. This surprisingly high value of the melting temperature for polyethylene may have not been observed for polyethylene crystallized by usual method and strongly suggests that the degree of the perfection of the crystals

formed in such way is very high and the crystalline size of the crystals may be significantly large.

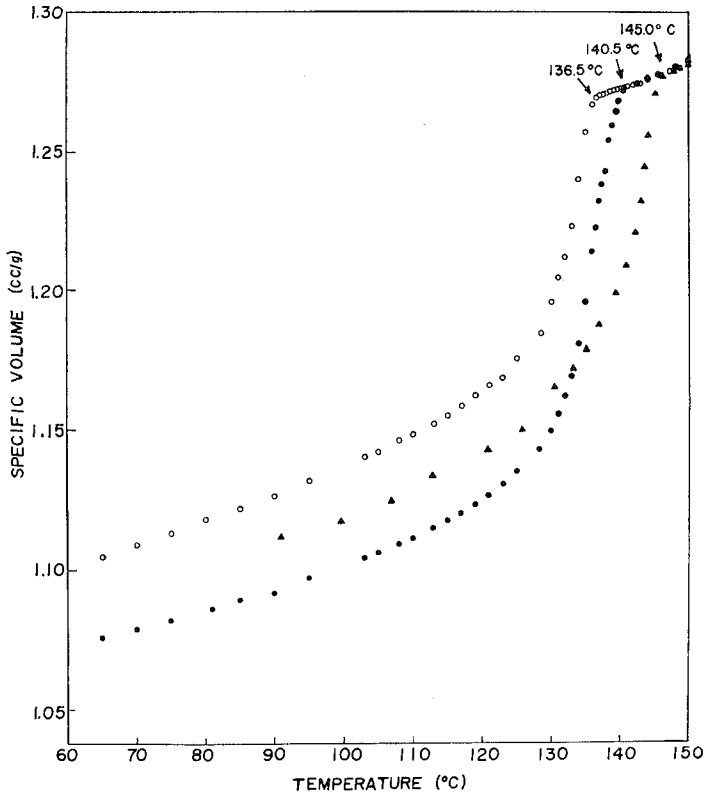

Fig. 10. Dilatometric melting curves for the Hostalen slowly cooled to room temperature from isotropic molten state (○) and from 6 times stretched and molten state (●). The melting curve obtained from the measurement during which the length of 6.0 times stretched sample was maintained at constant, is also shown for reference (▲).

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